Exhibit A

LABORATORY NOTEBOOK

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acrylic Family   (Principles of polymerization G. Odian 3rd ed. Wiley Interscience)

(P.311)

$$C = C \begin{array}{c} R_1 \\ | \\ | \\ R_2 \end{array}$$

$C = C \begin{array}{c} CONH_2 \\ | \\ | \\ H \end{array}$ acrylamide $\longrightarrow$ $\left(C - C \atop H \right)_n$ with $CONH_2$

$C = C \begin{array}{c} COOCH_3 \\ | \\ | \\ CH_3 \end{array}$ methyl methacrylate $\rightarrow$ $\left(C - C \atop CH_3 \right)$ with $COOCH_3$ $\boxed{PMMA}$

(MMA)

Process:
Solution, Suspension
emulsion
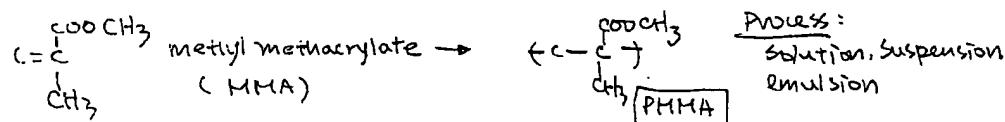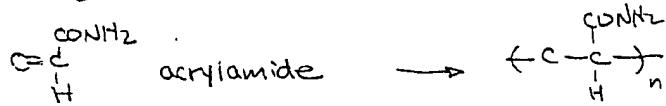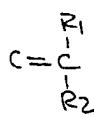
R_1	COOH	COOH	CN	Cl
R_2	H	CH$_3$	H	Cl
name	poly(acrylic acid)	poly(methacrylic acid)	polyacrylonitrile	poly(vinylidene chloride)
	water soluble	"		

R_1 - OCOCH$_3$

R_2 — H
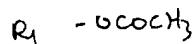
name   poly(vinyl acetate)
         water based paint

{ radical
{ ionic polymerization

chain polymerization

monomer : $C = C$ (vinyl species) . $\longrightarrow$ $\oplus C - C \ominus$, $\cdot C - C \cdot$

or $-\overset{O}{\overset{||}{C}}-$ $\longrightarrow$ $\overset{:O\ominus}{\underset{\oplus}{-C-}}$

(aldehyde , ketone)
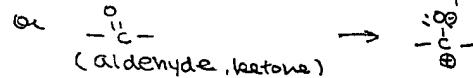
type of chain polymerization undergone by various unsat. monomers

monomer	type of initiation		
	radical	cationic	anionic
ethylene	+	−	+
~~vinyl ester~~, acrylate, methyl acrylate, acrylonitrile methacrylonitrile.	+	+	−
styrene, methylstyrene	+	+	+

eg $C = C_\delta^- \overset{O}{\underset{}{\overset{||}{C}}} - NH_2$ + $\oplus \oplus$

electron withdrawn group. $\rightarrow C = C_\delta^+ \cdots$
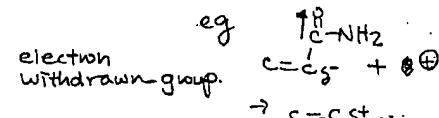
Ref: L Liang, X. Feng, J. Liu P.C. Rieke, G.E. Fryxell   Macromolecules 1998 31 7845—50.

Initiator:

ξ—OH + $(CH_3O)_3Si\,CH_2CH_2CH_2\,S-S-C-N\Big\langle{}^{CH_2CH_3}_{CH_2CH_3}$

          +

      NIPAAm / BisAAm
       UV, 254 nm

N,N'-(diethylamino) dithiocarbamoyl
propyl(trimethoxy) silane
    DATMS
    def 15, 16.

Reaction

      250ml 3 neck flask
     12g CPTMS + 4g SDDC + 100ml acetone
  3-chloropropyl trimethoxysilane, 97% Aldrich →^{purified} reduced distillation.

   $(CH_3O)_3Si\,CH_2CH_2CH_2-Cl$. <43868-6)

⎡ or   Run08. ⎤
⎢ 3-chloropropyl triethoxysilane 95% Aldrich   (C10-2) ⎢
⎣   [5089 7073 SIC 24070.   ⎦

SDDC:
Sodium N'-diethyl dithiocarbamate
    (
              $H_2N\,COO^-$

    CH_3CH_2 O
        $\searrow N-\overset{\|}{C}-0-S-S-Na$
    CH_3CH_2

⎡ Carbamate   ⎤   ⎡ dithiocarbamate ⎤
⎢   O   ⎢   ⎢   S   ⎢
⎢ $NH_2-\overset{\|}{C}-OR$ ⎢   ⎢ $NH_2-\overset{\|}{C}-SR$ ⎢
⎣   ⎦   ⎣   ⎦

Reaction:

$(CH_3O)_3Si(CH_2)_3-Cl$ + $Na-S-\overset{S}{\overset{\bullet}{\underset{}{}}}-C-N\wedge$

⎡ Lp: sodium diethyl dithio carbamate   ⎤
⎢   trihydrate   ⎢
⎢ $(Et_5)_2N-\overset{S}{\overset{\|}{C}}-S-Na\cdot 3H_2O$ ⎢
⎢   FW = 225.31   ⎢
⎢   mp = 95-98.5°   ⎢
⎣ hygroscopic.   22868-0 5g 17.55   ⎦

  → Nacl + $(CH_3O)_3Si\!\!\frown\!\!\frown\!\!S\!\!-\!\!\overset{S}{\overset{\|}{C}}-N\!\!\smile$
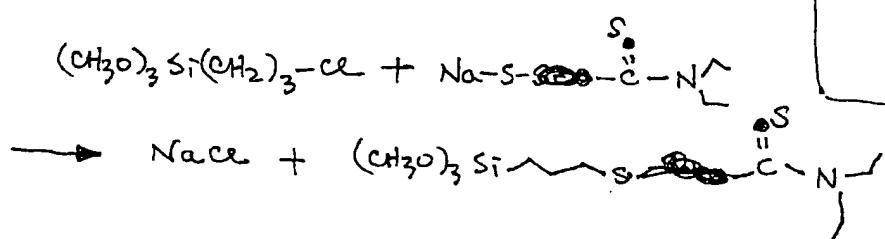
Redo surface polymerization.

polyacrylamide $\left(\begin{array}{c} C-C \\ | \\ C=O \\ | \\ NH_2 \end{array}\right)_n$. $\underline{MW}$

acrylamide $\overset{\,}{\underset{0.75\,g}{C}}=\overset{\,}{C}-\overset{O}{\overset{\|}{C}}-NH_2$. $\quad 71$ $\quad \dfrac{0.75g}{71} \sim 0.01\,mol.$
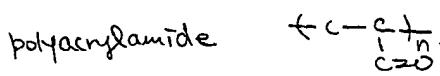
$\dfrac{1}{0.075}$: $\dfrac{1000}{75} = 13.$
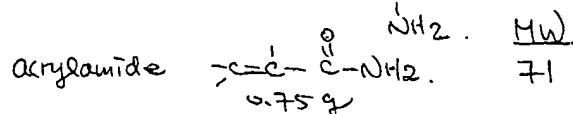
0.01 mol acrylamide/0.75 ml.

2,2' dipyridyl $\quad 0.036g$ $\quad \overset{MW}{156.19}\,(2.3\times10^{-4}\,mol) = \dfrac{0.01\,mol}{0.75\times10^{-3}\ell} = 1.3\,M.\,\,\underline{13M} \,\text{too high!}$

$1:3$
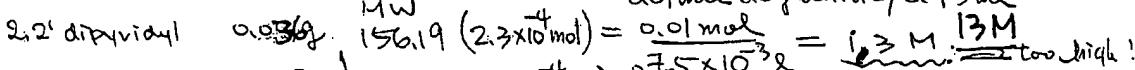
Cu(I)Cl $\quad 0.0065g$ $\quad 98.99\,(6.8\times10^{-4}\,mol)$

DMF $\quad 8ml$ $\quad\quad$ should reverse $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ Calc. ( )
$\quad\quad\quad 0.75$ $\quad\quad\quad\quad$ Cu(I)Cl : bipy = 1 : 3 ($10^{-4}\,mol$) $\quad$ M₀ : Cu(I)Cl $\quad$ (Wang, 1995)
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad = 10^{-4} : 3\times10^{-4}\,(mol)$ $\quad = 100 : 1$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad = 0.01g : 3\times156.19\times10^{-4}$ $\quad = 10^{-2}\,mol : 10^{-4}\,mol$

Rough estimation $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad = 0.01g : 0.04685g$ $\quad\quad = 0.71 : 0.01\,g$

What thickness means in this case

Assumption: density is const = bulk material

$d_4^{20} = 1.189$ For PAC 50% wt in H_2O.

$1.189 = \dfrac{1}{1/1.4/0.9}\dfrac{1+X}{2} \Rightarrow d_{PAC} \sim 1.37$

$\left(\begin{array}{c}\text{needed mole of}\\\text{monomers}\end{array}\right) = \dfrac{Ah\,d\,(total\,weight)}{71} = \dfrac{1\,cm^2 \times 1.37}{71}\,h(cm) = 0.019\times10^{-7}\,h(nm)$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \cong 2\times10^{-9}\,h(nm)\,\,moles.$

According to this, we can greatly reduce the amt of monomers from original recipe

ex: $h = 10^4\,nm\,(= 10\,\mu m)$ $\quad\quad$ | Assume densely packed · 1 molecule/nm^2
$\Rightarrow$ needed monomers $= 2\times10^{-5}\,mol$ $\quad$ | For $A = 1\,cm^2 = 10^{14}\,nm \Rightarrow 10^{14}$ # PAC $= \dfrac{10^{14}}{6\times10^{23}} = 1.7\times10^{-10}\,m$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ | $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \sim 2\times10^{-10}\,m$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ | DP $= 2\times10^{-5}\,mol/2\times10^{-10} = 10^5$ $\quad 10^5\times0.5 = 5\times10^4\,nm \sim O(10\,\mu m)$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ | $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (good agreement!)

For DMF 1ml. make 0.01 M acrylamide soln = 0.01 mol × 71 = 0.71 g

$0.01 = \dfrac{X\,mol}{10^{-3}\ell} \Rightarrow X = 10^{-5}\,mol.$ $\quad 10^{-5}\,mol \times 71 = 0.00071\,g.$

Roughly for DMF 10ml acrylamide 0.0071g $\Rightarrow \dfrac{0.0001}{0.01} = 10^{-2}\,M.$

Better soln: 0.1 M $\Rightarrow$ 10 ml DMF + 0.071 g acrylamide $\quad$ good enough for cover the whole surface!

$\overset{\,}{C}=\overset{\,}{C}-\overset{O}{\overset{\|}{C}}-NH_2$ $\quad MW = 71.1$

$\underset{CH_3}{\overset{\,}{C}}=\overset{\,}{C}-\overset{O}{\overset{\|}{C}}-NH-\underset{\underset{\underset{NH_2Cl}{CH_2}}{CH_2}}{CH_2}$ $\quad MW = 178.7$
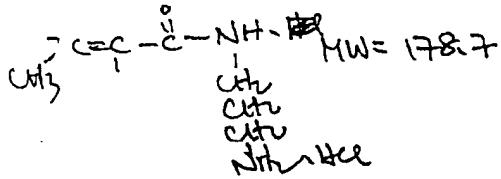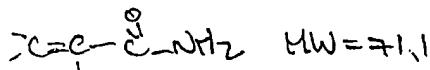
Objective: Repeat protocol exp 7 . For   N-(2-hydroxy propyl) ~~acryl~~ methacrylamide

$$C=C-\overset{\overset{O}{\|}}{C}-NH \longrightarrow$$

with CH_3 on lower left carbon, and CH_2, $CH-OH$, CH_3 chain on the N.

H]V6d N-(2-hydroxy propyl) methacrylamide [21442-01-3] MW 143.2 mp=67°   10g 121.25

$$H_2C=C\overset{CH_3}{\underset{COOCH_2CH_2OH}{}}$$ FW = 130.14   HEMA in 10ml DMF   0.1 mol = 13 g HEMA
                                                    d=1.073

    +

Cu(I)Cl (bipyridyl)$_2$ Cu(I)Cl (MW=99) 0.23g (0.0023 mol)   1
                            ~~1.45g~~
    +
                        bipyridyl ~~33g~~ (MW=156.19) 1.08g (0.0069 mol) 3

[structure: chlorine on benzene ring attached to surface]
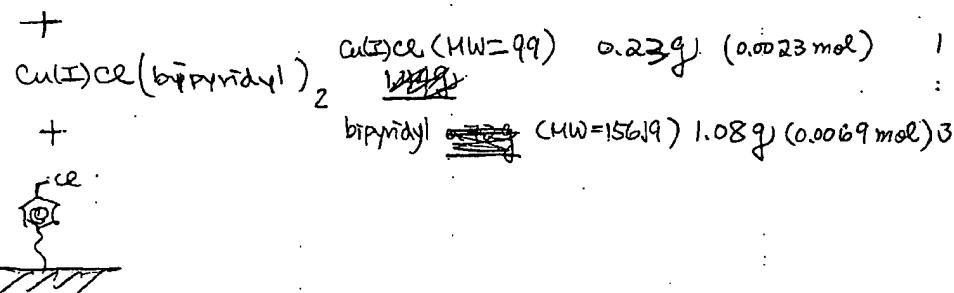
new materials.

    chlorophenyl propyl trimethoxysilane 30min 1% in acetone.
    Cl—⟨O⟩—Si(OCH$_3$)$_3$

    +

1h
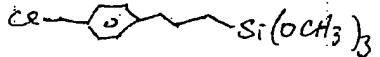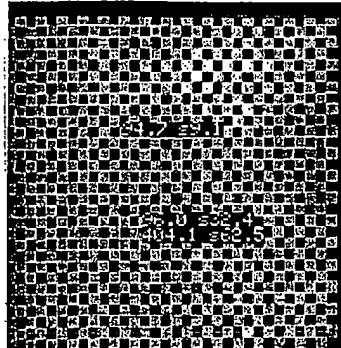
148.3 s39.6

[48..512] 06159914:CLS=
512 RWS=512 SIZ=27 VE=
83
09:53:02 S499-168,
soda lilme Affymetrix C
nfidential.

89.0 s77.2

106.2 s439.6
1541.8 s1527.6
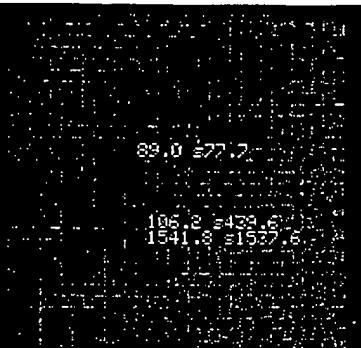
[64..18064] 06159915:CLS
=512 RWS=512 SIZ=27 VE=
.83
09:56:33 YC13-2 Affy
metrix Confidential.
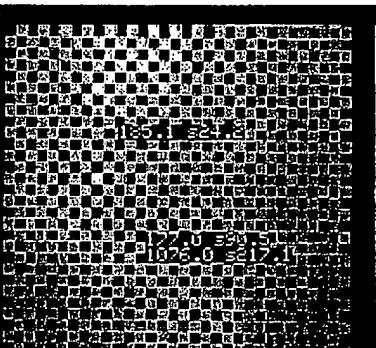
120.4 s17.6

[64..1440] 06159916:CLS=
512 RWS=512 SIZ=27 VE=.
83
10:00:26 S499-108, 70
nm, 500 rpm Affymetrix Co
nfidential.

81.1 s85.7

97.2 s391.9
1244.2 s968.6
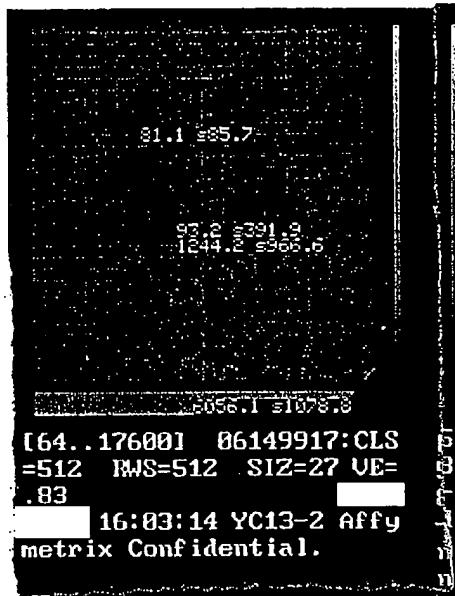
[64..17600] 06149917:CLS
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.83
16:03:14 YC13-2 Affy
metrix Confidential.

113.1 s44.2

128.5 s472.8
2557.5 s1493.0
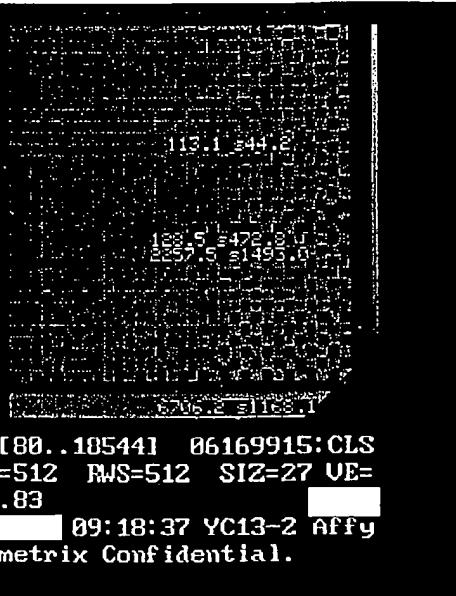
[80..18544] 06169915:CLS
=512 RWS=512 SIZ=27 VE=
.83
09:18:37 YC13-2 Affy
metrix Confidential.

17h

40h

Objective: AIBN — HEMA.

glass — 10 pieces.   Si substrates — 4 pieces.

Comment: last exp the thickness only reaches up to 10 nm. I think it's due to the low
(exp 11) surface coverage of AIBN layer (I forgot to work it in darkness, so the final
thickness is checked by Si wafer sample is only half of the thickness of exp 10.)

Improvement: This time I will work under dark and high conc. of initiator layer.

Sample	Initiator. Condition ( )
13-1	glass + AIBN/ toluene dark, Et₃N, rm temp in N₂ glove
13-2	bag. Starting) 4:00 pm
13-3	~ ''
13-4	''
13-5	''
13-6	''
13-7	''
13-8	''

HEMA
✗X✗.

DNA strands on pattern

work on condition
≥10⁻³
·20 to HEMA/DMF
65°C 24h.
degass.
free thaw 3 times

HEMA 40 ml
DMF 160 ml

Store in darkness.

deprotection
EtOH/EDA ethylene
(1/1) diamine
4h → w/
DI H₂O

hybridization
50 µM.
DNA target
—tag in 6XSSPE soln
(1h)
shake rm temp.
↓ 17 hr. (hyb)
scan 10 am
1st scan @
↓ 24 hr (total 40h)
(hyb)
2nd scan
↓
~~not scan~~

another protocol.
45°C 16h.

hyl

sample	hyp time(h)	hyp	backgd	fluorescein	hyp/bg	fluo/bg
e13-2	1	1244	88	6056	14.1	68.8
control 1	1					
control 2	1	362	66	171	5.5	2.6
e13-2/control		3	1	35	3	27

1244/362   88/66   6056/171   14.1/55   68.8/2.6

sample	hyp time(h)	hyp	backgd	fluorescein	hyp/bg	fluore/bg
e13-2	17	1542	89	6529	17.3	73.4
control 1	17	339	101	140	3.4	1.4
control 2	17	404	95	148	4.3	1.6
e13-2/control		4	1	45	5	50

sample	hyp time(h)	hyp	backgd	fluorescein	hyp/bg	fluore/bg
e13-2	40	2258	113	6706.2	20.0	59.3
control 1	40	225	94	99	2.4	1.1
control 2	40	318	93	114	3.4	1.2
e13-2/control		8	1	63	7	52

experiment 13
report on   file: e13-fluor.xls (thin's chang)
pHEMA initiated by AIBN
Fluorescence measured by Marc Glazer
Experiment condition: AIBN20h)- pHEMA(20h 65c) - DNA probes-hybridization
estimated pHEMA thickness: 5 nm (estimated by Si(100) ellipsometry; need further confirmed by XPS)

Comments for improvement: high standard deviation(ca 1500) -- surface film is not uniform enough -- ne
long hybridization time

Fluorescence signal ratio vs. Hyp time
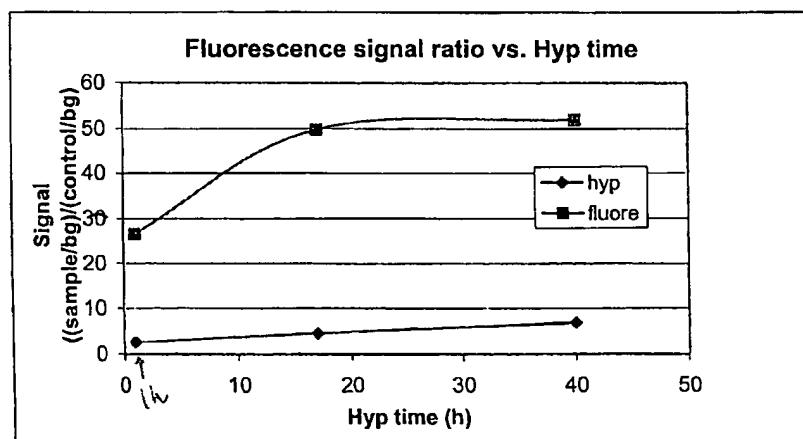
Signed....................................... Date........................

rxn
condition

13-9   "
            (same as
            ~~bad~~
            previous)

13-10   "

13-11   same
            batch
            but
            Si(100)

13-12   Si(100)

13-13   "

13-14   "